

# Monitoring the dispersion and agglomeration of silver nanoparticles in polymer thin films using Localized Surface Plasmons and Ferrell Plasmons

## Supporting information

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### S1. Silver thin film structural characterization

A silver thin film of 10 nm thickness and used as reference was fabricated by resistive evaporation onto a silica substrate in vacuum. The thickness was controlled with a calibrated microbalance.

The film was characterized by Atomic Force Microscopy (AFM) using a MFP-3D instrument from asylum research with a PPPNCH tip (10 nm tip radius) in tapping mode. The images show a continuous film, as exemplified in figure S1.

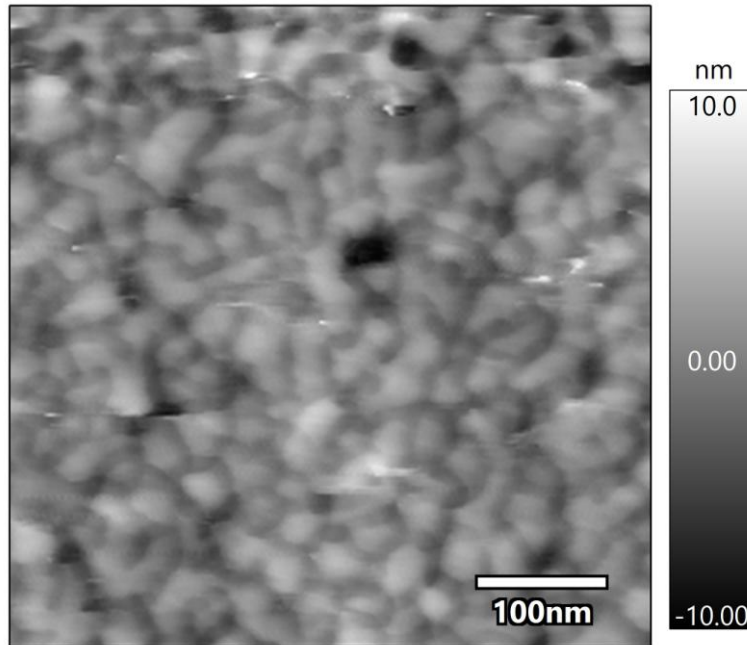


Figure S1: AFM image of the 10 nm Ag film.

The lateral size of the crystallites is of the order of 10 nm, the RMS rugosity is 1.3 nm. Only one single hole deep enough to reach the substrate has been observed for this film, cf. the center of figure S1. This means that the film is overall continuous with touching crystallites. If some holes between neighboring crystallites are still present, their percentage in the surface area is small as they cannot be evidenced with a 10 nm tip.

These observations agree with literature values, where similarly fabricated films were shown to percolate at  $\sim 4$  nm equivalent thickness and to be fully continuous at 9 nm equivalent [1].

## S2. Cross sectional microscopy

In order to visualize the dispersion of nanoparticles in the polymer film, cross-sectional cuts of samples were produced using a Dual Beam Helios 660 Focused Ion Beam milling (FIB) machine at the Electron Microscopy Laboratory at the National Laboratory of Nanotechnology (LNNano/CNPEM) in Campinas, Brazil. The lamellas were prepared using the alternative method for polymeric cross section samples production proposed by F. Rivera et al. [2].

In a first step a lamella of 30  $\mu\text{m}$  x 22  $\mu\text{m}$  and 12  $\mu\text{m}$  depth is removed from the sample. This is then thinned in regions of 1.5  $\mu\text{m}$  by varying the ion beam current from 770 pA to 18 pA until a region thin enough for TEM analysis ( $\sim 40$  nm) is obtained.

Scanning Transmission Electron Microscopy (STEM) cross-section analysis shows that the NPs are implanted into the polymer matrix, as shown in Figures S2 and S3.

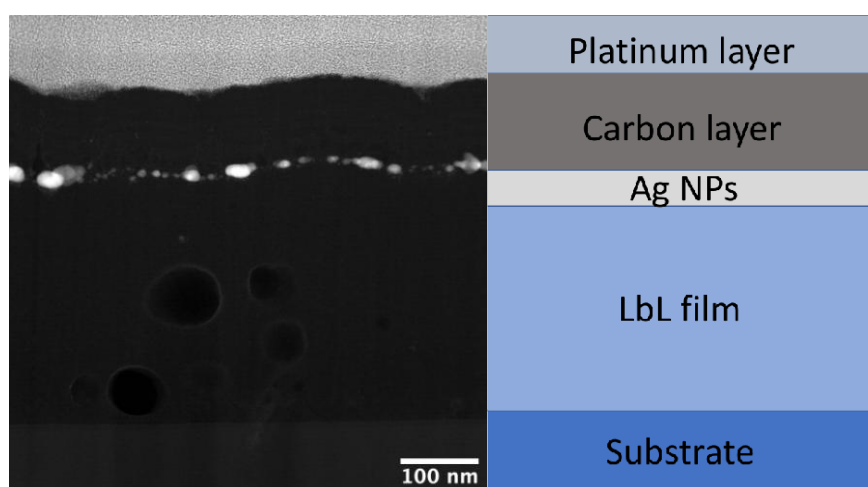


Figure S2: Cross sectional STEM image of a (PAH/PSS)150 sample with low Ag dose. The sample was covered by layers of amorphous carbon and platinum for FIB preparation.

Figure S2 shows a STEM micrograph of a sample in which Ag NPs were deposited for 40 minutes. In this projection view coalescence cannot be excluded, but no continuous film is formed yet. The dark circles at the bottom of figure S2 represent thinner regions that were damaged during the thinning process.

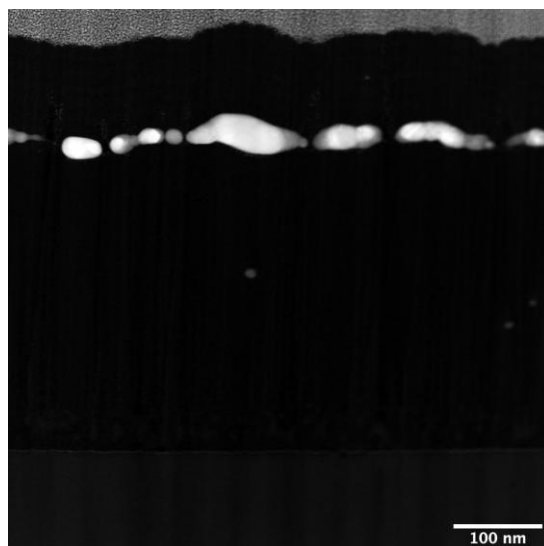


Figure S3: STEM micrograph of a (PAH/PSS)<sub>150</sub> sample with high Ag dose.

Figure S3 shows a STEM micrograph of a sample in which Ag NPs were deposited for 110 minutes. Increasing the NP loading does not lead to further dispersion in the polymer but to coalescence and the successive formation of a continuous film.

#### References

- [1] Maaroo, A. and Sutherland, D. S. *J. Phys. D: Appl. Phys.* **43**(40), 405301 (2010).
- [2] Rivera, F., Davis, R., and Vanfleet, R. *Microsc. Microanal.* **19**(4), 1080–1091 (2013).